



Date of Application and filing Complete Specification: Feb. 10, 1958

No. 4276/58.

Application made in United States of America on Feb. 13, 1957.

Complete Specification Published March 2, 1960.

Index at acceptance: — Class 100(2), L1, LA6A.

International Classification: —B44b.

COMPLETE SPECIFICATION

Method of Regenerating a Glass Etching Bath

We, CORNING GLASS WORKS, a Corporation organized under the Laws of the State of New York, United States of America, of Corning, New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to improvements in the selective etching process of chemically machining or sculpturing glass described in Specification No. 699,897. It is more particularly concerned with hydrofluoric acid etching solutions used in the process of the said specification and regeneration of such solutions to extend their useful life and provide for substantially continuous etching operations.

15 Briefly the process of Specification No. 699,897 involves forming within a glass article a design comprising crystallites selected from the class consisting of a lithium silicate, barium disilicate and an alkali metal fluoride, while leaving the remainder of the glass article unaffected, and thereafter treating the glass with a dilute aqueous solution of hydrofluoric acid to dissolve preferentially one portion of the glass. In glass articles containing such crystalline designs that portion of the glass containing crystallites is etched or dissolved by hydrofluoric acid at a different rate than is the remainder of the glass. The ratio of these different etching rates may be as great as 50 to 1 depending on such factors as glass composition, type of crystallite, and concentration, composition and temperature of the acid etching solution. In general optimum etching ratios are provided by lithium-containing glasses having a lithium silicate type of crystallite formed therein. For purposes of illustration then, the present invention is described more particularly with reference to this type of glass wherein a crystallite containing glass etches more rapidly than a corresponding clear glass.

The process is capable of wide use in pro-

ducing, from glass, intricately shaped and/or precisely patterned articles such as panels for flush printed circuitry, printing plates, screens and instrument panels. It is also extremely valuable in producing accurately perforated glassware, an outstanding example being glass aperture masks for colour television receiving tubes. Such masks consist of a thin glass sheet having thousands of accurately dimensioned and spaced holes per square inch of glass surface.

It has been apparent however that success in many of these applications ultimately depends on availability of a standardised continuous operation whereby an etching acid solution is used over an extended period of time for successively etching like glass articles in accordance with an established schedule. Experiments directed to this end have shown however that both glass etching rates, and the ratio of such etching rates in the clear, and crystallite containing portions, vary widely with concentration and composition of the hydrofluoric acid etching solution. A standardised process then requires some means of maintaining the etching solution at a constant concentration and composition.

The obvious expedient of using fresh solution is impractical because of the cost factor as well as the problem of waste acid disposal. Hence an effective means of solution regeneration becomes highly desirable and it is the primary purpose of this invention to provide such means.

It was initially thought that an acid etching bath could be regenerated by simply adding sufficient hydrofluoric acid to compensate for that consumed in etching, that is in reacting with the oxide constituents of the glass, and crystallites therein, to form corresponding fluorides. However attempts to employ a bath regenerated in this manner revealed that the etching rate of the faster etching, crystallite-containing portion of a glass continuously decreased even though the apparent acid concentration of the bath was maintained con-

BEST AVAILABLE COPY

stant. Experimental studies demonstrated that hydrofluosilicic acid (H_2SiF_6) was being produced during solution of silica (SiO_2), a major glass constituent, and that a substantial portion of the apparent hydrofluoric acid present was therefore relatively ineffective for etching purposes. We then found that it was necessary to maintain a constant concentration of free hydrofluoric acid that is hydrofluoric acid exclusive of that present as hydrofluosilicic acid, in order to maintain a standard etching rate for crystallite-containing glass.

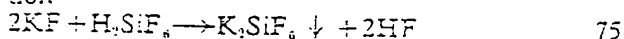
This however proved to be only a partial solution of the problem since it then became apparent that, as an etching bath ages by being regenerated and re-used in this manner, the differential etching rate decreases. That is to say the clear glass and crystallite-containing glass portions of an article tend to etch at more nearly the same rate in such a bath even though the etching rate of the latter remains constant. We have now found that this most undesirable and unexpected change in differential etching rate is, surprisingly, also occasioned in large part, if not entirely, by the accumulation of hydrofluosilicic acid in the etching bath. While no good explanation can be offered for this unexpected difference in behaviour between crystallite-containing glass and clear glass, the need for controlling concentrations of both hydrofluoric acid and hydrofluosilicic acid in regenerated etching solutions is quite apparent.

An obvious remedy is to replace periodically a sufficient portion of the used acid with a suitable mixture of fresh acid and water to maintain the hydrofluosilicic acid at a low concentration and the free hydrofluoric acid concentration at the desired initial level. While this process is effective, it is of limited use and highly uneconomical since increasingly large amounts of otherwise utilisable hydro-

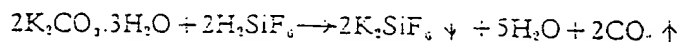
fluoric acid are discarded each time. It is apparent then that some method of controlling etching solution composition by neutralising the hydrofluosilicic acid without affecting the hydrofluoric acid solution is needed and a further and more specific purpose of this invention is to provide such a method.

The present invention provides a method of controlling the etching of a silica-containing glass in a hydrofluoric acid solution which comprises regenerating the etching solution by neutralising at least a part of the hydrofluosilicic acid formed and adding sufficient fresh hydrofluoric acid to restore the initial concentration of free hydrofluoric acid in the solution.

Any compatible, soluble salt, the metal ion of which forms a relatively insoluble silicofluoride and soluble fluoride, may be used for neutralising the hydrofluosilicic acid. We have found however that potassium salts are particularly effective for the purpose. Care must be exercised in selecting the salt employed so as not to introduce into the bath an ion which either will interfere with subsequent etching or will have a detrimental influence on the equipment used. Nitrate and sulphate ions, for example, should be avoided where the corresponding acid formed by such ions may have a corrosive effect. Potassium fluoride may be used in accordance with the following reaction



and introduces only fluoride ions already present in the bath. However this salt is rather expensive to use and necessitates making allowance for the amount of acid which it adds to the bath. For these reasons it is frequently preferable to use potassium carbonate, either anhydrous or hydrated, since, in accordance with the following reaction



the carbonate ion decomposes and may therefore be disregarded as far as subsequent effect on either the process or equipment is concerned.

Ideally, during operation of the etching bath, the acid solution is continually circulated through a filtering arrangement with metered amounts of the precipitating solution being added, the exact amount being controlled by a device sensitive to the hydrofluosilicic acid concentration in the solution. The silicofluoride salt formed is removed as the material is pumped through the filter and, while the filtered liquid is circulated back to the etching bath, metered amounts of hydrofluoric acid are added, the exact amount again being controlled by a device sensitive to the hydrofluoric acid concentration. For most purposes however an elaborate arrangement of this sort and the precise control which it affords are quite unnecessary. In general then it is suffi-

cient to add periodically a pre-determined and measured amount of precipitating agent to the etching bath and circulate the entire bath through a filter with an intermediate settling bed being employed if desired. Conveniently a dual bath arrangement is provided so that one bath may be used while the other is being regenerated.

We have further found that for various reasons it is both unnecessary and undesirable to completely remove the hydrofluosilicic acid present in the etching bath. Thus when this acid is completely precipitated the regenerating bath frequently etches quite erratically. The reason for this has not been clearly ascertained. It is strongly suspected however that a super-saturated solution is in some way formed and that salts capable of blocking etchings are thereafter deposited on any glass introduced into the regenerated bath. In accordance with one theory potassium ions

remain in the regenerated solution and tend to gather on a new glass surface to interfere with etching. A second proposed theory suggests that the solubility of certain metal fluorides formed during etching, such as lithium fluoride, is related to the presence of hydrofluosilicic acid and that the solubility of such salts is so altered by complete removal of this material as to form a super-saturated solution. Regardless of the explanation however, our experiments have indicated the desirability of maintaining at least a small positive concentration of hydrofluosilicic acid at all times in a regenerated etching bath.

In etching processes, and particularly in the perforation of glass, it is frequently desirable to provide a controlled taper to the perforation. For example the successful operation of certain aperture or shadow masks in cathode ray tubes depends on providing the apertures or perforations with a controlled taper so that electrons are properly transmitted and not "clipped" or absorbed when they approach the mask perforations at a slight angle. Inasmuch as the differential etching ratio can be varied by varying the concentration of hydrofluosilicic acid, it is therefore possible to correlate this acid concentration with the etching ratio so as to provide any desired degree of taper on the etched perforations. Thus, in producing aperture masks by etching glass having a differential etching ratio of about 35 to 1 in 10% hydrofluoric acid, we have found it convenient to operate with etching solutions in which the hydrofluosilicic acid concentration, expressed in terms of SiO_2 , is maintained within a concentration range equivalent to 2 to 5% SiO_2 . In general higher concentrations of hydrofluosilicic acid produce too great a taper, unduly lower the etching ratio and tend to produce an uneven surface on the etched glass, while lower concentrations do not provide adequate taper.

We have also found that in order to obtain the optimum results from a regenerated etching bath it is desirable to agitate the bath during etching and to maintain it at a temperature of about 25°C . or higher. With lower temperatures and/or a still bath there is a tendency for the etching ratio to vary erratically, probably due to partial retention of insoluble etch products on the glass. Agitation of the bath may be satisfactorily accomplished either by mechanically stirring the bath during etching, or by forcibly applying the acid to the surface being etched as by spraying.

By way of further illustrating our invention the process of regenerating an etching bath used in the production of glass aperture masks is described. Thin sheets of glass having the following approximate composition, 79.5% SiO_2 , 10% Li_2O , 5% K_2O , 4% Al_2O_3 , 1% ZnO , and minor amounts of photosensitizing and fining agents, were given a suitable photothermal treatment as described in Specification No. 699,897, to produce in the glass a desired pattern of crystallites for selective etching purposes. The glass sheets, thus treated, had a differential etching ratio of about 35 to 1. They were then successively suspended above an etching bath containing about 54.3 U.S.A. gallons of 10% hydrofluoric acid solution and etched for a pre-determined time (by splashing acid up against the down-surface of the glass plates) by a suitable rotary paddle arrangement to provide the desired tapered apertures in the sheets. During etching the metal fluorides LiF , KF , AlF_3 , and ZnF_2 , or complexes thereof, were formed, and the etched silica was converted into hydrofluosilicic acid. Once the bath reached a concentration of such acid equivalent to 5% of SiO_2 , etching was discontinued and 40 pounds of $2\text{K}_2\text{CO}_3 \cdot 3\text{H}_2\text{O}$ added to the etching bath. The resulting slurry, containing precipitated potassium fluosilicate was filtered through a cloth filter and returned to the etching system with sufficient fresh 60% hydrofluoric acid and water to maintain the bath at a relatively constant volume and the free hydrofluoric acid concentration at approximately 10%.

The precipitate removed by filtration was neutralised and discarded. Alternatively it might be dried and recovered as a by-product. This process is of particular value in the production of aperture masks since there is virtually no limit to the number of times the bath may be regenerated. Furthermore, as indicated above, the bath is maintained constantly within the desired limits of hydrofluosilicic acid concentration for the production of suitably tapered perforations.

WHAT WE CLAIM IS:—

1. A method of controlling the etching of a silica-containing glass in a hydrofluoric acid solution which comprises regenerating the etching solution by neutralising at least a part of the hydrofluosilicic acid formed and adding sufficient hydrofluoric acid to restore the initial concentration of free hydrofluoric acid in the solution.
2. A method as claimed in Claim 1 wherein the etching solution is regenerated to maintain substantially constant etching rates and etching ratio during etching of a silicate glass which has been photothermally treated to render a portion of the glass more soluble than the remainder of the glass.
3. A method as claimed in Claims 1 or 2 wherein the etching solution is regenerated to etch tapered perforations in a glass article by maintaining the hydrofluoric acid concentration constant and the hydrofluosilicic acid content within a range corresponding to the degree of taper.
4. A method as claimed in any one of the preceding claims wherein the hydrofluosilicic

BEST AVAILABLE COPY